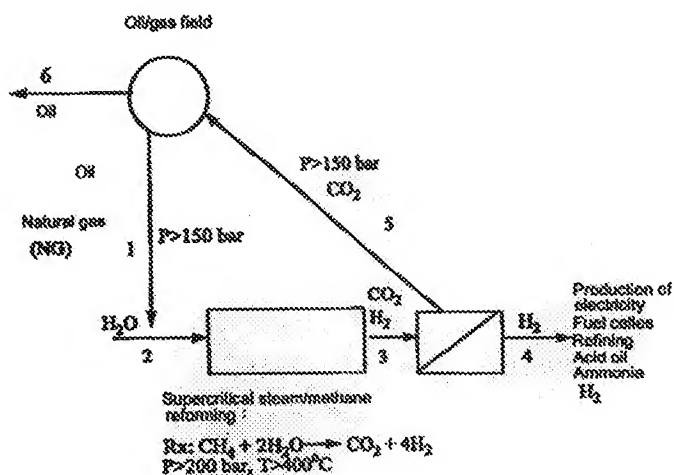




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/NO99/00283 (22) International Filing Date: 15 September 1999 (15.09.99) (30) Priority Data: 19984296 16 September 1998 (16.09.98) NO (71) Applicant (for all designated States except US): DEN NORSKE STATS OLJESELSKAP A.S [NO/NO]; N-4035 Stavanger (NO). (72) Inventor; and (75) Inventor/Applicant (for US only): OLSVIK, Ola [NO/NO]; Haukv. 18, N-7562 Hundhammeren (NO). (74) Agent: BRYN & AARFLOT AS; P.O.Box 449 Sentrum, N-0104 Oslo (NO).	(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i> <i>In English translation (filed in Norwegian).</i>	

(54) Title: METHOD FOR PREPARING A H₂-RICH GAS AND A CO₂-RICH GAS AT HIGH PRESSURE

(57) Abstract

The present invention concerns a method for preparing a CO₂-rich gas stream for injection purposes or deposition, and a hydrogen rich gas stream, the method comprising the following steps: a) natural gas and H₂O are fed into a one-step reforming process for preparing a gas mixture comprising CO₂ and H₂ under supercritical condition for water from about 400 °C to about 600 °C, and pressure from about 200 to about 500 bar in the reforming reactor; b) the gas mixture from a) is separated into a H₂-rich and a CO₂-rich gas stream, respectively. The invention also comprises use of CO₂-rich gas stream for injection into marine formations, and use of H₂-rich gas stream for hydrogenation, as a source of energy/fuel in fuel cells and for production of electricity.

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Method for preparing a H₂-rich gas and a CO₂-rich gas at high pressure.

The present invention comprises a method for production of a CO₂-rich gas for injection purposes or to be deposited, and a hydrogen-rich gas, and use thereof.

5 It is commonly assumed that the greenhouse effect and the climate on earth have are closely connected to human made emissions of CO₂. These emissions are primarily formed by combustion of coal and hydrocarbons, i.a. by generation of heat and electric power. A desireable goal is therefore to reduce the emission of CO₂ to the atmosphere.

10 It is known art to reduce the emission of CO₂ from combustion of natural gas, e.g. by gas reforming and shift technology for preparation of a mixture consisting of hydrogen and carbon dioxide. These components are then separated, whereafter hydrogen is used as fuel in a gas turbin and carbon dioxide is deposited after compression to desired pressure. The deposition can be made on the
15 bottom of the sea or in geological reservoirs. The reservoirs can also contain hydrocarbons. The above mentioned technique is i.a. described in Teknisk Ukeblad No. 16, page 8, 1998.

Known art comprising gas reforming and shift technology as described above is very expensive and at the same time gives less energy yield than a
20 conventional, modern gas power plant.

US 3,652,454 describes preparation of CO₂ and H₂ from a gas stream containing CO by an improved continuous catalytical shift reaction at high pressure. The reaction takes place i one or more shift reactors at a superatmospheric pressure of from 35 to 250 atmospheres, and a temperature between 287°C and
25 537°C. The patent does not describe reforming of natural gas.

From EP 0 000 993-A1 it is known a method for preparation of ammonia by means of a primary and a secondary catalytic reforming of an hydrocarbon stream at superatmospheric pressure. From the primary catalytic reforming the ratio of steam to carbon is from 2.5 to 3.5, the pressure is from 30 to 120 bar and
30 the temperature out of the reactor is from 750 to 850°C. From the secondary catalytic reforming the content of methane is from 0.2 to 10 % by weight on a dry

basis and the ratio of hydrogen to nitrogen is from 2.2 to 2.7. To the he secondary reforming there is added an excess of air for preparing a gas with a higher content of methane, i.e. at a lower temperature, and/or a lower steam ratio and/or a higher pressure . In the above mentioned EP patent CO₂ is removed at a low
5 pressure by taking out hydrogen at an elevated pressure for further use by the preparation of ammonia.

EP 0 289 419 describes catalytic steam reforming of hydrocarbons for preparing hydrogen i an ammonia process. The catalytic steam reforming takes place at a pressure from 25 to 120 bar, a temperature from 800 to 1000°C and at
10 at ratio steam:carbon of 1.8-2.5. The process is operated in such a way that there are less than 0.3% impurities in the H₂-rich gas which is to be used for production of ammonia. The present invention allows a higher content than 0.3% of CO, CO₂ and CH₄ in the H₂-rich gas stream.

CA 868,821 describes preparation of synthesis gas by steam reforming of
15 hydrocarbons in a gas and a liquid at 50-250 absolute atmospheres, preferably 160 abs. atm. for production of ammonia and methanol.

Known art does not deal with a one step prosess for production av CO₂-rich gas and H₂-rich gas under supercritical conditions for water, where a CO₂-rich gas mixture is taken out at an elevated pressure in the interval from 20 to
20 200 bar for injection or deposition i marine formations. The present invention involves reduced compression costs by deposition or injection in marine formations because the CO₂-rich gas mixture is taken out at an elevated pressure.

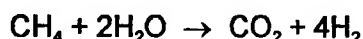
The present invention comprises a method for preparing a CO₂-rich gas stream and a hydrogen rich gas stream, the method comprising the following
25 steps:

- 30
- a) natural gas and H₂O are fed to a one-step reforming process for preparing a gas mixture comprising CO₂ and H₂ under supercritical conditons for water;
 - b) the gas mixture from a) is separated into a H₂-rich and a CO₂-rich gas stream, respectively.

Further the temperature in the reforming reactor is from about 400°C to about 600°C, and the method is also characterized by a pressure in the reform-

ing reactor from about 200 to about 500 bar. The CO₂-rich gas stream from the separation unit is at a pressure in the interval from 20 til 200 bar. I the present invention the mixture in the reforming reactor may be passed over a catalyst bed. The reforming can also be carried out without catalyst. The present invention
5 also concerns use of the CO₂-rich gas stream prepared according to the previously mentioned method, where the CO₂-rich gas stream is injected into marine formations. Further, the invention comprises use of the H₂-rich gas stream prepared according to the invention, where the H₂-rich gas stream can be utilized for hydrogenation, i the production of electricity and as a source of energy / fuel in
10 fuel cells.

The following reaction takes place during the reforming:



The reforming reactor is operated at supercritical conditions for water. The temperature in the reforming reactor is from about 400°C to about 600°C and the
15 pressure in the reforming reactor is from about 200 to about 500 bar. It is an object of the present invention that CO₂ is separated from the gas stream at a pressure of at least 20 bar and maximum 200 bar before being injected into marine formations or by deposition. The reforming reaction takes place over a suitable catalyst bed. The reforming can also take place without catalyst in the reforming
20 reactor. It is also an object of the present invention to use H₂ made according to the method of the invention, for hydrogation, and for production of electricity. Use of H₂ as a source of energy / fuel in fuel cells is further comprised by the present invention.

CO₂ is an acid gas, and the most widely used method to separate the
25 mentioned gas from other non-acid gas molecules is absorption. During absorption the different chemical properties of the gas molecules are utilized. By contacting the gas mixture with a basic liquid the acid gases to a high degree will be dissolved in the liquid. The liquid is separated from the gas and the absorbed gas can the be set free either by altering the composition of the liquid or by altering
30 pressure and temperature. For separation of CO₂ mainly aqueous solutions of alcoholamines are used. The absorption is taking place at a relatively low temperature and high pressure, while stripping of the gas from the liquid is carried

out at a relatively high temperature and low pressure. To liberate CO₂ from the amine phase in the stripping unit stripping steam is usually used. If the partial pressure of CO₂ in the gas into the absorber is high, e.g. higher than 15 bar, it is possible to obtain high concentrations in the amine phase, and a large part of absorbed CO₂ can be set free in the stripping unit at elevated pressure, e.g. 5-8 bar.

By the use of one or more semipermeable membrane units it is possible to achieve that molecules of different molecular weight and different properties permeate the membrane at different velocities. This principle can be utilized to separate gases. For the gas mixture in question membranes can be selected where H₂ permeates rapidly, whereas CO₂ permeates slowly, whereafter a separation-in-part of the different gas components is achieved. By combining solid membranes and liquid membranes it is also possible to achieve a rapid permeation of CO₂, while H₂ is kept back. It can be difficult to achieve complete separation of the different gas components by using different separation methods. This is especially the case by use of membranes. For gas mixtures which are going to be burned, a partly separation of hydrogen and CO₂ will be sufficient.

In the present invention it is desireable to deposit out-separated CO₂. Large amounts of CO₂ can be deposited according to various methods, of which the three most interesting are deposition at very deep oceans, deposition in deep water reservoirs and deposition in oil reservoirs wherein the gas at the same time functions as drive agent for enhanced oil recovery. The two last mentioned storage methods are operated commercially. In these storage forms the CO₂ gas has to be brought to high pressure for transport in pipelines to a deposition well and further to injection. The injection pressure will vary, but could be in the range 50 to 300 bar. If the CO₂ gas can be separated from the H₂/CO₂ mixture at an elevated pressure, significant compression work can be avoided, and this is the case in the present invention.

The invention is further elucidated on Figure 1. Natural gas (1) is passed from an oil/gas field, and blended with H₂O (2) before the mixture is passed to reforming at supercritical conditions. Produced synthesis gas (3) is separated at high pressure into two streams, a CO₂-rich stream (5), which is injected into an

oil/gas field, and a H₂-rich stream (4), respectively. The H₂-rich stream is further used for hydrogenation, as a source of energy in fuel cells, and for production of electricity.

5 **Example 1:**

The example concerns one or more membrane units wherein the CO₂-rich gas can have a pressure approximately equal to the partial pressure of CO₂ into the separation unit, as shown in Table 1 below.

10

Table1

Total inlet pressure on the separation unit (bar)	Partial pressure of CO ₂ out of the separation unit (bar)
200	40
250	50
300	60

Example 2:

Supercritical conditions occur at pressures above 220 bar and temperatures above 374°C.

15

In this example it is described at which conditions supercritical conditions occur in the present reactor.

The relationship between temperature and pressure in the reactor in the present invention is as shown in Table 2. Supercritical conditions occur in the reactor when the values of pressure and temperature are higher than shown in

20

Table 2.

Table 2

Pressure (bar)	Temperature (°C)
1100	354
750	356
500	362
300	368
220	374

Relationship between temperature and % fraction H₂O at 220 bar is shown in table 3. Supercritical conditions occur in the reactor when the values for temperature and % fraction H₂O at a pressure of 220 bar are higher than shown in Table 3.

Table 3

% fraction H ₂ O (P =220 bar)	Temperature (°C)
0.95	372
0.85	365
0.75	353

The relationship between pressure and % fraction H₂O at a temperature of 374°C is shown in Table 4. Supercritical conditions occur in the reactor when the values for pressure and % fraction H₂O at 374°C are higher than shown in Table 4.

Table 4

% fraction H ₂ O (T= 374°C)	Pressure (bar)
0.95	300
0.85	400
0.75	1000

Claims

1. Method for preparing a CO₂-rich gas stream for injection purposes or deposition, and a hydrogen rich gas stream,
5 characterized in that the method comprises the following steps:
 - a) natural gas and H₂O are fed into to a one-step reforming process for preparing a gas mixture comprising CO₂ and H₂ under supercritical conditons for water;
 - b) the gas mixture from a) is separated into a H₂-rich and a CO₂-rich gas
10 stream, respectively.
2. Method according to claim 1,
characterized in that the temperature in the reforming reactor is from about 400°C to about 600°C.
15
3. Method according to claims 1-2,
characterized in that the pressure in the reforming reactor is from about 200 to about 500 bar.
- 20 4. Method according to claims 1-3,
characterized in that the CO₂-rich gas stream is present at a pressure within the interval from 20 to 200 bar.
5. Method according to claims 1-4,
25 characterized in that the mixture in the reforming reactor is passed over a catalyst bed.
6. Method according to claims 1-5,
characterized in that the reaction in the reforming reactor is carried out
30 without a catalyst.
7. Use of a CO₂-rich gas stream according to claim 1 for injection into marine formations.

8. Use of a H₂-rich gas stream made according to claim 1 for hydrogenation.

9. Use of a H₂-rich gas stream made according to claim 1 as a source of energy / fuel in fuel cells.

5

10. Use of a H₂-rich gas stream made according to claim 1 for production of electricity.

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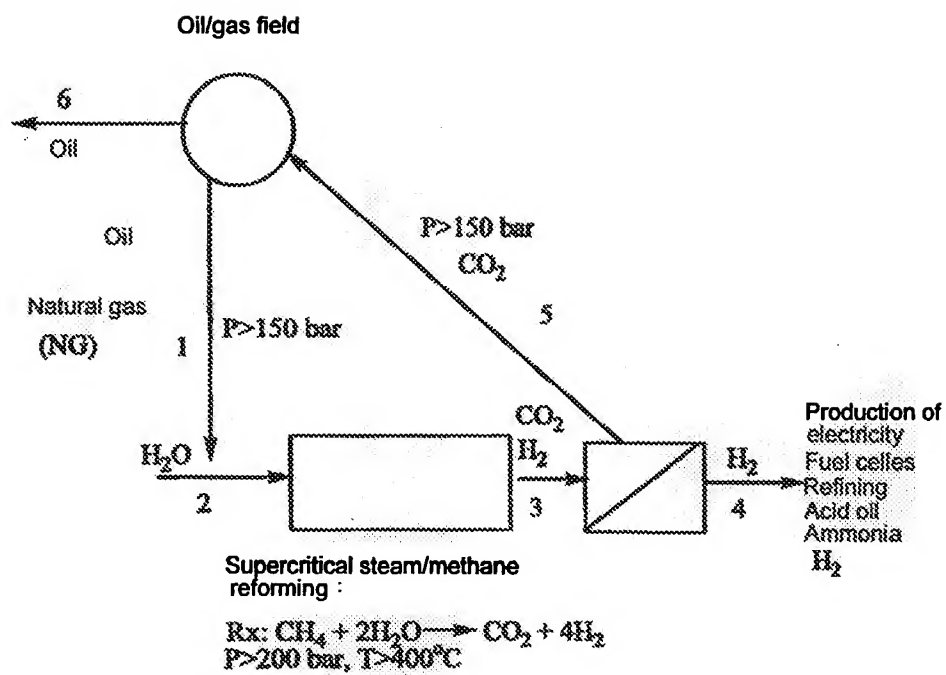


Figure 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 99/00283

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C01B 3/48, C01B 31/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

FULLTEXT, EPODOC, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 868821 A (GIORGIO PAGANI), 20 April 1971 (20.04.71), page 3, line 9 - line 12, claims --	1-6
X	WO 9829333 A1 (EXXON CHEMICAL PATENTS INC.), 9 July 1998 (09.07.98) ---	1-6
X	US 5714132 A (AKHILESH KAPOOR ET AL), 3 February 1998 (03.02.98), column 1, line 11 - line 14; column 2, line 38 - line 44; column 5, line 21 - line 26 --	1-6
A	US 3652454 A (ALLEN M. ROBIN ET AL), 28 March 1972 (28.03.72) ---	1-6

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

10 March 2000

Date of mailing of the international search report

14-03-2000

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INTERNATIONAL SEARCH REPORT

International application No.
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Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See extra sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 1 - 6

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO99/00283

- I. Claims 1-6 relate to a process for producing a CO₂- and a H₂-rich gas.
- II. Claim 7 relates to the use of a CO₂-rich gas for injection in marine formations.
- III. Claim 8 relates to the use of a H₂-rich gas for hydrogenation.
- IV. Claim 9 relates to the use of a H₂-rich gas as a source of energy in a fuel cell.
- V. Claim 10 relates to the use of a H₂-rich gas for electricity production.

The special technical feature of Group I is a process for producing the gases H₂ and CO₂. The special technical features of Group II-V involve different applications of the gases H₂ and CO₂. The gases H₂ and CO₂, produced according to claim 1, are well known products. There is a reference in each of the independent claims 7-10 to the process for producing these known products. However, the production process does not give the products any new characteristics, therefore the reference made in claim 7-10 does not involve the features in claim 1. The group of inventions is not so linked as to form a single inventive concept under PCT Rule 13.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

02/12/99

PCT/NO 99/00283

Patent document cited in search report			Publication date	Patent family member(s)	Publication date
CA	868821	A	20/04/71	NONE	
WO	9829333	A1	09/07/98	AU 6646498 A EP 0950017 A NO 993228 A US 5904880 A	31/07/98 20/10/99 30/08/99 18/05/99
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US	3652454	A	28/03/72	NONE	